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Relationship Between Appearance and Protective Durability of Coatings: A Literature Review

T. Nguyen, B. Collins, L. Kaetzel, J. Martin, and M. McKnight

U.S. DEPARTMENT OF COMMERCE
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ABSTRACT

Research in building materials has increasingly been focused upon procedures for service life prediction. For coatings, improved service life prediction will aid in the effective selection and use of materials and in the development of cost-effective maintenance strategies. However, quantitative measures of degradation are essential in predicting service life. Standard procedures are available to quantitatively measure small changes in the appearance properties of coatings, one of the two primary functions of coatings, the other being protection. However, quantitative measurements of early changes associated with the protective function usually are not possible. Hence, the objective of this report is to ascertain, based upon the literature, whether changes in appearance properties of coatings can be used to predict changes in the protective properties of the film. It was concluded, that for the most part, changes in appearance properties are not related to changes in the protective properties of a coating film.

Key words: coatings; appearance; service life; durability; paint; measurement

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1. INTRODUCTION

In recent years, it has been increasingly recognized that data on the service lives of building materials and components are essential to achieving longevity through the effective selection, use and maintenance of materials [Masters, 1987]. This recognition has stimulated several international conferences on the durability of building materials [Frohnsdorff and Horner, 1981; Masters, 1985; Sereda and Litvan, 1980; Sneek and Kaarresalo, 1984] and has led or is leading to the development of several standard procedures on predicting service life [e.g., ASTM; Masters and Brandt, 1987]. In particular, for coatings, several researchers have studied procedures to predict service life [Martin and McKnight, 1985; Rehfeldt, 1987] and recently an entire symposium was devoted to the measurement and prediction of durability of organic coatings; many of the papers were published in Progress in Organic Coatings, Volume 15, 1987.

The service life of coatings is usually defined in terms of parameters associated with one of the two primary functions of coatings, protection and appearance. Many factors can affect these parameters, such as environmental exposure, paint formulation, substrate properties, substrate movement, film thickness, age, and surface preparation [Bierwagen, 1987]. Factors associated with protection properties of coating films usually affect the bulk properties of the film and the film/substrate interfacial properties, while factors associated with appearance properties are generally associated with the upper bulk and surface characteristics. Early changes in bulk or interfacial properties are more difficult to quantify than those associated with the surface [Croll, 1987]. Thus, the question arises as to whether changes in the surface properties of a coating film can be used to predict changes in the protective properties. For example, rate of change of one of the appearance properties, i.e., gloss, has been shown to correlate with the square root of the photoinitiation rate for an acrylic-urethane and an acrylic-melamine coating [Gerlock, 1985]. Hence, the main objective of this review is to determine whether, from the literature, a technical basis exists for using changes in appearance properties to predict the longevity or service life of the protective properties of a coating film.

2. APPEARANCE OF COATING FILMS

The appearance of a coating depends on both the surface and bulk properties of the coating. As described by Hunter (1987), four major things can happen to light when it falls upon an object: 1) specular reflection at the first surface (associated with gloss), 2) scattering within the materials (associated with diffuse reflection), 3) absorption within the material (largely responsible for color) and 4) regular transmission through the object (associated with clarity). These ideas are represented in figure 1 for a pigmented coating. The fraction of the light that is specularly reflected depends on the roughness of the

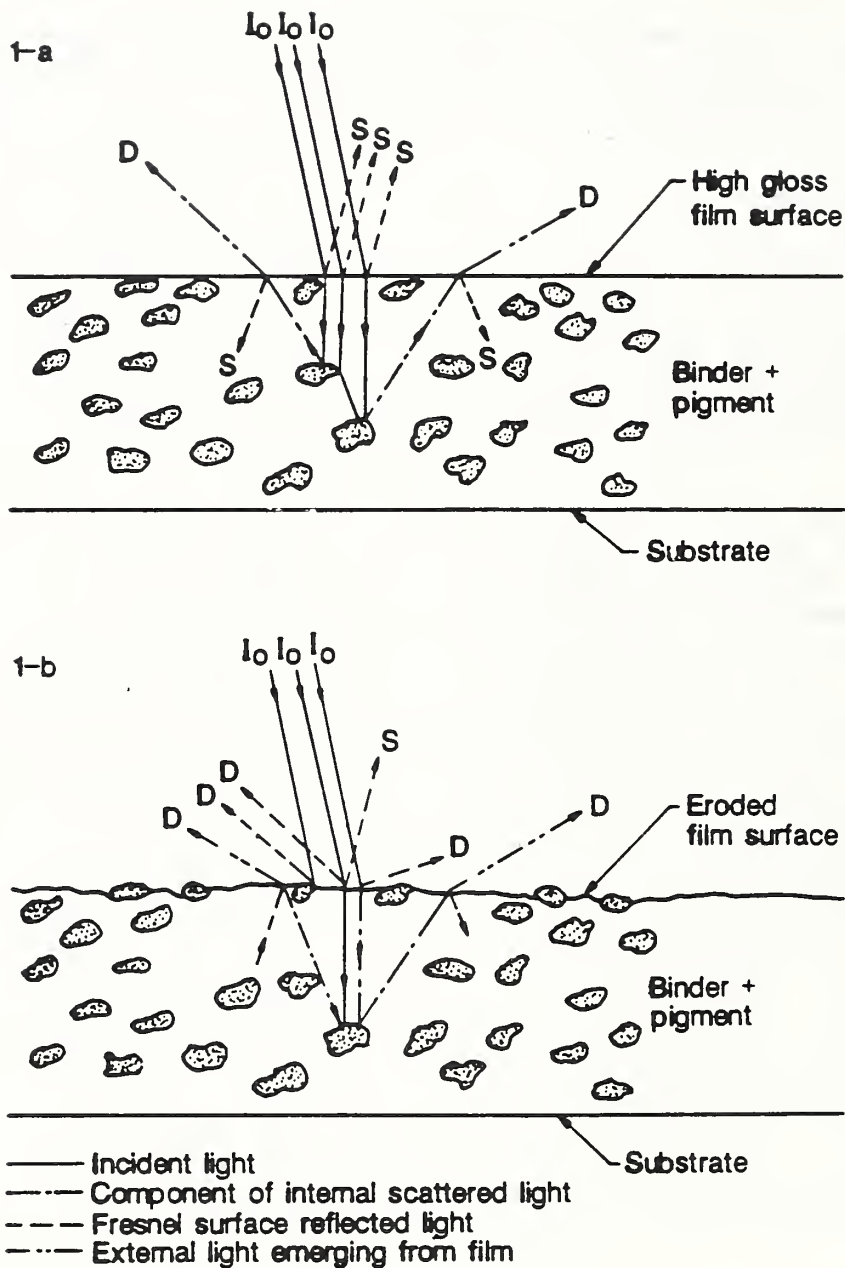


Figure 1. Diagrams showing light striking a paint film; 1-a is a high gloss surface, 1-b is an eroded surface after exposure when the surface reflectance is partially diffuse. Light incident on the surface is designated I_0 , light specularly reflected, S , and light diffusely reflected, D [Johnson-Feller and Osmer, 1977].

surface and increases with increasing smoothness of the surface. Specular reflection is responsible for a glossy appearance. As the surface of the coating weathers and roughens, light is scattered from the surface in many directions; this scattered light is added to the observed diffuse reflectance and causes a lighter appearance of the coating.

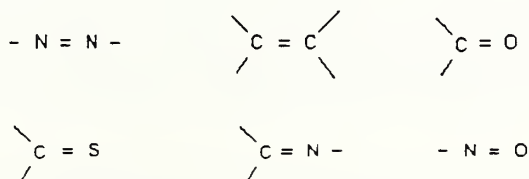
The major portion of light enters the film, is refracted because of the different indices of refraction of the mediums and then is multiply reflected or partially absorbed by the pigment particles. This process of multiple reflection and refraction thoroughly diffuses the light and returns much of it to the surface where it leaves in all directions. This is called diffusely reflected light and the process of diffusing the light is called scattering. Because the diffusely reflected light and the scattered light from the surface are combined, color and gloss attributes of a coating are not completely independent.

Factors needed to describe color include those describing the visual sensitivities of the observer or receptor and the spectral characteristics of the light source. These factors are described in the Appendix. Hunter [1936] described six different types of gloss and how to measure them; currently designated as specular, distinctness of image, contrast, haze, sheen and macroscopic [Billmeyer, Jr., 1985]. Standard methods to characterize and measure color and gloss are described in the Appendix.

2.1 CHEMISTRY OF COLOR AS APPLIED TO ORGANIC COATINGS

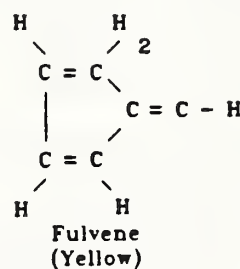
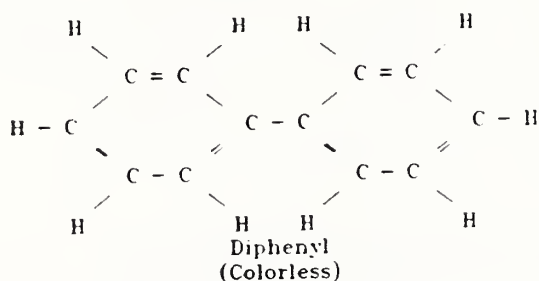
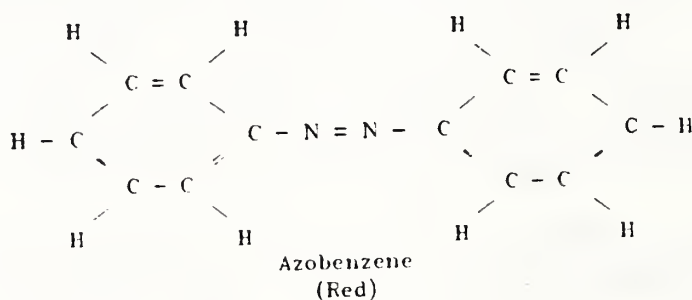
To aid in understanding the mechanisms which cause change in the color of a coating, a brief discussion of the causes of color is presented. Nassau [1983] describes 15 causes of colors; however, three appear to be responsible for most of the color in coatings, namely: 1) organic materials containing a conjugated system of alternating single and double bonds, 2) inorganic materials containing transition metals and 3) materials in which charge transfer occurs.

Although early development of organic dyes and pigments was based on the idea of chromophores [Sklar, 1937], as illustrated below,



and an alternation of single and double bonds, there were problems with this approach. The color does not depend on the number of these alternations but rather on the structure of the entire molecule. For example, fulvene, which is yellow, has three alternations, whereas diphenyl, which does not absorb in the visible but only in the ultraviolet, has six alternations. As the limitations to the chromophore approach became obvious, an approach based on resonance and molecular orbital theory was developed.

Typical colored organic compounds are represented below.



Some colored inorganic pigments contain metal transition ions with unpaired electrons in d or f orbitals. Explanations of the color of these materials can be obtained by applying crystal field theory. The unpaired electrons can absorb light by ligand-field controlled transitions that do not involve change in the valence state. The quantity of energy that is absorbed is controlled by the number and symmetry of the ligands and the strength of the ligand field. Changes in the ligand may result in changes in color as noted below:

Ligand Field Colors of Some Chromium Compounds

<u>Anion</u>	<u>Divalent Cr</u>	<u>Trivalent Cr</u>
Bromide	White	Olive green
Chloride	White	Violet
Fluoride	Green	Green
Iodide	Gray	Black
Oxalate hydrate	Yellow	Red
Sulfate hydrate	Blue	Violet

The third mechanism of color, charge transfer, involves the tendency of an electron to move from one transition metal ion to another within the material, resulting in a temporary change in the valance state of both ions. This mechanism is the cause of the black or dark colors of many transition metal oxides, e.g., Fe_3O_4 ; the bright blue color of sapphire (Al_2O_3 with impurities of both Fe^{+2} and Ti^{+4}); and lead chromate (commonly called chrome yellow).

3. APPEARANCE CHANGE DURING SERVICE

Appearance change in coatings during service is often described as change in one or more of the following engineering properties: 1) color (including fading, darkening, yellowing and bronzing), 2) gloss, 3) chalking, 4) resistance to dirt pick-up, and 5) pigment separation [Johnston-Feller and Osmer, 1977]. These changes are usually associated with surface deterioration of a coating film. Although deterioration such as blistering, corrosion, peeling and cracking affect the appearance of the film, these kinds of deterioration also involve changes in the bulk of the coating and at the coating/substrate interface. Hence, changes in these properties are usually not included in discussions of appearance deterioration and will not be included in this discussion.

Often, more than one of these properties changes as a result of service exposure. Although in a visual inspection, one tends to combine the effects into an overall assessment, information on the mechanisms causing an appearance change and on the extent of the change can be obtained by using a series of carefully chosen quantitative instrumental measurements. For example, by measuring reflectance with and without the specular contribution, before and after washing, the cause and magnitude of the appearance change can be determined [Johnston-Feller and Osmer, 1977]. A diagnostic protocol for such measurements is shown in table 1.

It is apparent from table 1 that changes in color, gloss and chalking are the three primary factors contributing to appearance

Table 1. Analysis of Spectrophotometric Reflectance Curve
Diagnosis Scheme¹

<u>Type of Appearance Change</u>	<u>Differences in Reflectance from Unexposed Specimens</u>
1.a Pigment fading	Increase in R_c^I in region of maximum absorption for each pigment; little or no change in region of maximum reflectance (minimum absorption).
1.b Pigment darkening	Same as 1.a except a lowering of R_c^I in region of maximum reflectance.
2.a Decrease in gloss	Uniform decrease in S at all wavelengths.
2.b Increase in gloss	Uniform increase in S at all wavelengths.
3. White chalking	Uniform increase in R_w^D at all wavelengths.
4. Dirt accumulation	Decrease in R_w^D uniform with respect to wavelength except in presence of white in chromatic chalking.
5. Bronzing	Nonuniform change in S with respect to wavelength.
6. Resin or vehicle yellowing	Decrease in R_c^I in short wavelength region.
7. Internal separation of pigment from binder	Same as 1.a in symptoms, but represents an addition of white pigment.

Notation: R = reflectance from 400-700 nm, 20 nm resolution;
S = specular reflectance
Superscripts: T = total reflectance;
D = diffuse reflectance
Subscripts: U = unexposed
C = exposed and cleaned
W = exposed, but uncleaned

change of the surface of a coating system during exposure. These properties and the factors that contribute to the changes of these properties during service are discussed in the following sections.

3.1 FADING

Fading is the gradual decrease of color intensity resulting from exposure of colored paints to sunlight or to weather [van Beek, 1986; Johnson-Feller, 1986]. The principal mechanisms of fading are the photodegradation of the tinting pigment by ultraviolet (uv) radiation and the reactions of organic pigments with radicals formed upon absorption of short-wavelength light by the polymeric binder or colorless additives [van Beek, 1986]. For a given paint, the rate of fading depends on the conditions of exposure. Tropical regions tend to cause faster fading than temperate zones. The presence of moisture, acid or alkaline conditions, also appears to accelerate the fading of some pigments; for example, fading of a set of automotive paints as a result of outdoor exposure was found to be influenced by SO_2 concentration [Hoffmann and Vogel, 1976]. The resistance to fading (i.e., light fastness) of a pigment can be affected by the presence of other pigments with which it is mixed. For example, alizarin lake is protected by the presence of TiO_2 when exposed to uv [Johnson-Feller, 1986]; however, some other pigments are more resistant to fading at full strength than in tints [Mone, 1968]. Another example is the fading of phthalo blue, which alone shows good fastness to light but fades when mixed with red iron oxide [Hunter, 1975]. On the other hand, an inclusion of a small amount of zinc oxide pigment, probably due to its high uv absorption, in rutile TiO_2 used for tinting purpose can improve tint retention [Madson, 1967]. In addition, the lightfastness of some organic pigments has been found to be related to their particle size distribution [Hafner, 1975].

The main causes of fading are summarized below.

- 1) The pigments used are not sufficiently fast to light.
- 2) The pigments are sensitive to acidic and basic materials, and to air and moisture in the atmosphere. For example, traces of acid can destroy the color of pale shades made with ultramarine blue [Moser, 1975]; similarly, Prussian blues turn brown due to alkaline attack, e.g. from lime cement, etc. [Fuller, 1967]; SO_2 causes color change in chrome greens [Schurr, 1975].
- 3) Chemical and physical interactions between the pigments and the binder may cause fading. Not every pigment or dye is equally fast in every binder [Hafner, 1975].

- 4) Chemicals released during curing may also cause fading. For example, certain phthalocyanine greens are susceptible to fading due to formaldehyde released from synthetic resins during stoving [Hess, 1979].
- 5) Fading is also caused by chalking in at least two ways; fading of colors occurs in admixture with TiO_2 after chalking has commenced, and colors appear to fade when the surface is covered with powdery white pigment [Fuller, 1968].

3.2 YELLOWING AND DARKENING

Yellowing becomes apparent in white and pale shades but is not common for materials with dark pigments. The principal elements that cause yellowing are light, heat and contaminants. Yellowing due to light is associated with the unsaturation of the fatty acids used [Hill and Hall, 1973]. Thus, linseed type alkyds, which contain an appreciable amount of linolenic acid, yellow most intensely. The semi-drying oils such as soya bean and safflower contain little or no unsaturated acid and are used to formulate the non-yellowing alkyds. The most well known contaminant that causes yellowing is ammonia. Oleoresinous or alkyd paints used on refrigeration plants or in hairdressing establishments yellow very rapidly. This yellowing is believed to derive from the interaction of 1,4-diketones, the auto-oxidation product of the paint film, and ammonia to give substituted pyrroles [O'Neill, et al., 1962]. Yellowing due to contaminants is most severe in the absence of light because the compounds responsible are readily bleached by light. Furthermore, yellowing of certain binders, principally those derived from drying oils, can result from tobacco smoke or from decomposition products of fat and oils as in the kitchen. Most frequently the yellowing and darkening of exposed paint films is due to the contamination by dust, especially in urban and industrial atmospheres.

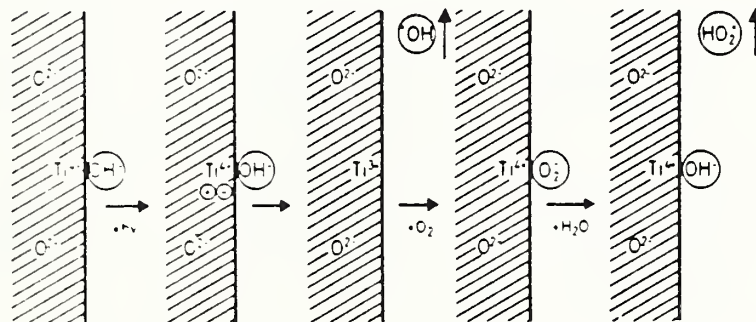
Mold (mildew), algae, and bacteria growths developed on poorly ventilated, damp and warm places are a cause of darkening of all sorts of coatings. Molds belong to the family of fungi, which requires nutrients, such as carbohydrates, nitrogen, sulfur, potassium and phosphorous for their development. Algae are green chlorophyll-containing organisms which are developed by photosynthesis, while bacteria also need food for development but multiply only in a damp environment. Molds can attack most paints including oil base paints, and can be found both inside and outside even in Antarctic regions. Mold spores are easily spread and settle on paint, often before the paint is fully hardened, and may remain dormant for long periods under rather dry conditions; above a certain humidity, they are activated again. While darkening is more obvious on white and light tint

films, mold, algae and bacteria attack can also be unsightly on colored paints. Although early failures resulting from these attacks are discolorations of the paint films, continuing growth of these materials on paint films will lead to severe damage of the films and corrosion of metals [Hess, 1979].

3.3 CHALKING

Chalking is the condition of a coated surface characterized by the overall presence of a friable powder or chalk that can be removed by light rubbing [Volz, et al., 1973-74]. Generally, chalking appears on whites or light tints and is the result of photochemical breakdown of the surface layer of the binder with subsequent release of pigments. (Bronzing is associated with similar deterioration in dark colored paints.) The most well known chalking pigment is the anatase grade of TiO_2 ; a paint based on this pigment and exposed to the weather suffers rapid loss of gloss followed by heavy chalking.

The chemistry of chalking in paints containing TiO_2 is well understood [Volz, 1973-74; Braun, 1987]. It is based on the formation of hydroxyl and peroxy radicals, formed by the interaction between the pigment, uv light, oxygen and water. The reaction sequence is shown below.



The absorption of uv radiation by the coating initiates the degradation process. TiO_2 acts as a catalyst for the degradation in a photo-stable binder. Photosensitive binders are degraded in two ways, catalytically by TiO_2 and directly by uv. It is generally accepted that the chalking related to the catalytic action of TiO_2 does not occur if water is excluded. Water adsorbs on TiO_2 to form hydroxyls which become radicals after

absorbing uv light. Oxygen is required to form peroxy radicals. Hydroxy and peroxy radicals activate, oxidize and degrade the organic binder. The process and severity of chalking depends on the susceptibility of the binder to the radicals and photoactivity of the pigments. For more durable resins, the photoactivity of the pigment predominates, whereas in less durable resins, the pigment acts in a protective manner.

A proposed model of chalking processes for TiO_2 pigmented coatings, which was confirmed using electron scanning microscopy, is illustrated in figure 2 [Kaempf, et al., 1974]. On exposure of TiO_2 -pigmented binders to weathering, uv degradation of the binder starts uniformly over the entire surface of the film. However, the chalking process caused by the photoactivity of the TiO_2 pigment takes place only in the immediate vicinity of the pigment particles. Figure 2 shows that the TiO_2 particles on the surface of the coating still adhere relatively firmly to the film through the so-called binder "pedestal" rather than being completely exposed, even after advanced degradation.

Pigments which are resistant to chalking include rutile TiO_2 , red oxide of iron, antimony oxide and carbon black. These materials are thought to absorb uv and convert the radiant energy to heat; thereby, protecting the binder from degradation [Larson, 1972].

As mentioned above, the main causes of chalking are related to the use of unsuitable pigments and the photo sensitivity of the binder. For example, chalking is a characteristic of some polymers even when pigmented with rutile TiO_2 or other pigments which are not usually associated with chalking. The epoxy resins are of this type. Water aids in degrading such a paint film by leaching or washing away binder-oxidized products and pigments [Sullivan, 1972]. The repeated condensation of water on the film followed by drying also accelerates the onset of chalking. The mechanism is associated with microcracks formed as a result of the contraction and swelling of the film resulting from cyclic dry and wet periods. Although loss of material amounting to 5 μm of film thickness per year is not considered to be detrimental to the qualitative properties of the film [Gabriel, 1968], it has been claimed that the measurement of early weight losses resulting from chalking can be used to predict the erosion of paints in their later life [Ritter, 1971].

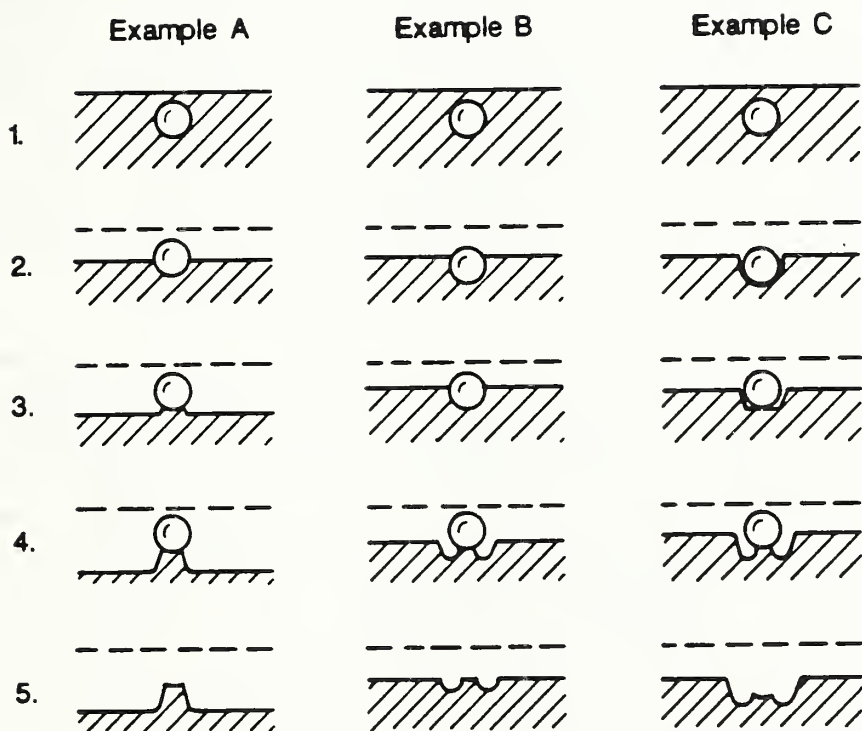


Figure 2. Schematic representation of degradation processes during the weathering of TiO_2 -pigmented binders. Sample A - Stabilized rutile pigment in binder of low light stability; Sample B - Stabilized rutile pigment in binder of high light stability; Sample C - Unstabilized rutile or anatase pigment in binder of high light stability [Kaempt, 1974].

3.4 LOSS OF GLOSS

Loss of gloss or gloss retention is one of the most commonly used criteria to assess the appearance durability of glossy paints, particularly in the automotive industry [Blakely, 1985; Gerlock, 1985, et al.; Bauer, et al., 1987, et al.; McEwen, 1987]. However, its use as a predictor of the degradation of low gloss paints is questionable [Rehfeldt, 1985]. Specular gloss measurements are quantitative and sufficiently sensitive to follow the process of degradation. Although gloss loss has been indicated as a significant predictor of the onset of fading and chalking [Ritter, 1971; Church, 1965], only recent work using an advanced analytical technique (electron spin resonance spectroscopy) has provided a mathematical relationship between the rate of gloss loss and the photodegradation rate of binders [Gerlock et al., 1982 and 1985; Bauer et al., 1987]. However, ESR was found to be 200 times more sensitive for detecting early degradation than typical gloss measurements. Although the relationship was developed for acrylic type resins, other limited results [Croll, 1987] suggest that similar patterns may exist for other types of resins. The relationship between gloss loss and rate of degradation has led to a proposal to use ESR as a method to predict rapidly the durability of a coating based on very short exposure [Gerlock et al., 1985; Bauer et al., 1987].

It is generally recognized that there is a relationship between gloss and surface roughness [McEwen, et al., 1987; Simpson, 1978], and that a glossy paint contains a layer of lightly pigmented binder above a more densely pigmented layer [Murley and Smith, 1970]. Such a film reflects the incident light specularly. Any disturbance of the surface smoothness, such as fine rivelling or pigment aggregates, will cause scattering and decrease the ratio of specular reflectance to diffuse reflectance, i.e., gloss will be reduced. Although surface roughness, surface porosity and film thickness initially affect the gloss of a film [Hess, 1979], the most common cause of loss of gloss during exposure is the loss of the binder which results in an increase in surface pigment concentration [Colling and Dunderdale, 1981; Kaempt, et al., 1974]. There has been much debate whether the increase in surface pigment concentration during aging is due to loss of binder on the surface (erosion theory) or due to loss of binder beneath the coating surface which results in differential contraction of the surface layer (contraction theory) [Colling and Dunderdale, 1981].

A mechanism of gloss loss has been proposed recently and is shown in figure 3 [Gerlock, et al., 1985]. As seen in figure 3, the rate of gloss loss is a complex function of resin and binder properties. As for chalking, the main factor that causes gloss loss is the photodegradation of the binder [Gerlock, et al., 1985]. However, Gerlock found that the degradation is mainly due to the photooxidation of the binder and very little to the

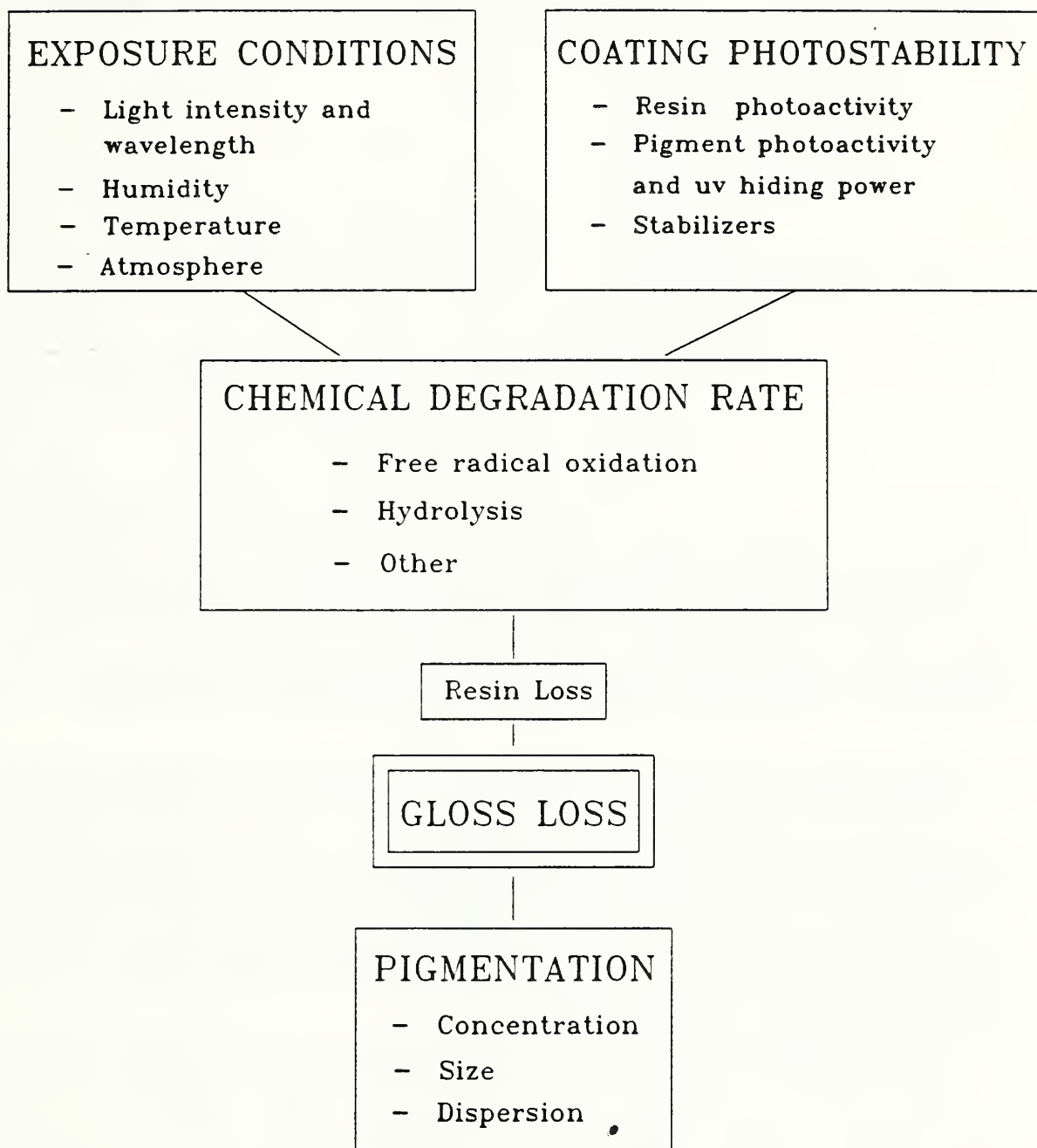
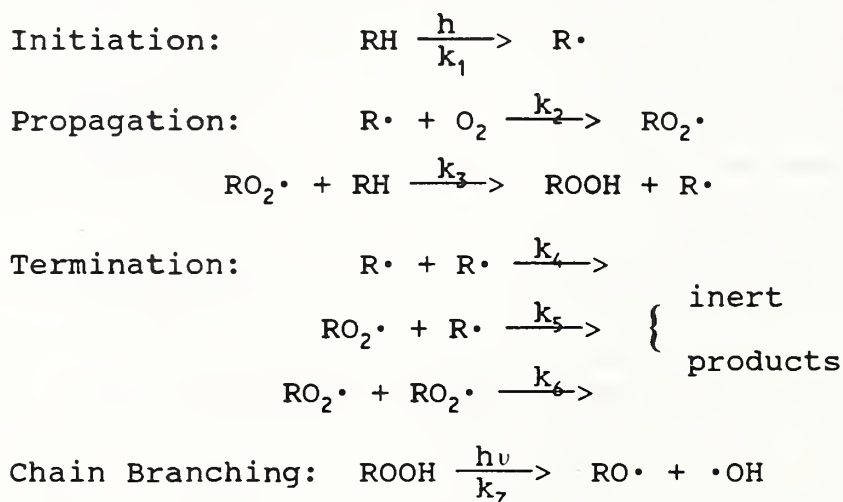


Figure 3. Mechanism of gloss loss [Gerlock, et al., 1985].

photoactivity of the pigment used. Thus, the intensity and wavelength of the uv radiation are the important factors controlling the rate of gloss loss. The fundamental process underlying the photooxidation of a polymer is a free radical chain mechanism whose scheme is shown below [Vink, 1983].



This reaction results in loss of materials and a more polar surface. The presence of moisture also enhances the loss of gloss [Ellinger, 1977]. Other types of degradation, such as hydrolysis and chemical changes triggered by pollutants, that cause loss of the binder have also been recognized [Gerlock, et al., 1985; Ranby and Rabeck, 1983]. The mechanism of degradation of the binder that results in chalking and gloss loss in a TiO_2 pigmented coating was presented in the chalking section.

4. RELATIONSHIP BETWEEN APPEARANCE AND PROTECTIVE SERVICE LIVES

From the preceding section, it was shown that mechanisms and processes that can lead to deterioration of the surface of a coating film and to changes in appearance are reasonably well understood. This section will address the question as to whether this information can be used to predict changes in protective properties of a film, i.e., in the bulk and at the coating/substrate interface.

4.1 CURRENT CRITERIA TO ASSESS DURABILITY OF COATING SYSTEMS

Service life is defined as the length of time, after installation, that a material or system fulfills its service requirements. For some applications, e.g., automotive, appearance stability may be the major requirement, whereas for other applications, protection of the substrate may be the major requirement. The degradation event or events that lead to the loss of durability of a coating system are schematically illustrated in figure 4; this is a modification of the diagram

taken from G. P. Bierwagen [1987]. Current methods to assess the durability of a coating are tabulated in table 2.

Table 2. Objective and Subjective Measures of Durability¹

<u>Objective measures</u>	<u>Subjective measures</u>
Contact angle	General appearance
Color difference	Checking/flaking
Gloss difference	Fade of color
Weight loss, film thickness change	Percentage substrate exposed
Optical properties in visible range - transmittance and reflectance	Attack through to substrate
Conductivity, impedance	Numerical ratings of appearance
ESR, NMR	Percentage area damaged
FTIR, ATR, drift, PAS, transmittance	Hazing
XPS (ESCA), SIMS, Auger	Peeling
Thermal properties: TG, DMA, TGA	
Barrier properties to gases and liquids	
Acoustic emission	
Mechanical properties	

¹From Bierwagen, G.P., Prog. Org. Coat., 15 (1987) 179.

It is interesting to note that almost half of these methods are related to the surface appearance of a coating.

A recent, exhaustive study of methods to quantify the degradation of a coating found that procedures are available to measure surface deterioration. Croll [1987] concluded that among the physical techniques examined, contact angle and gloss offer the most promise. These are both quantified versions of visual evaluation tests. Among the analytical techniques, which comprise most of the techniques listed in table 2, ESR is the only technique that provides quantitative information on the rate of surface degradation (by photolysis). Techniques to measure bulk degradation e.g., hydrolysis, have not yet been quantified. However, under well-controlled experiments, it appears that other analytical techniques such as FTIR [Bauer, et al., 1984] and XPS [Storb and Bock, 1985] may be used to determine degradation rates.

¹From Bierwagen, G.P., Prog. Org. Coat., 15 (1987) 179.

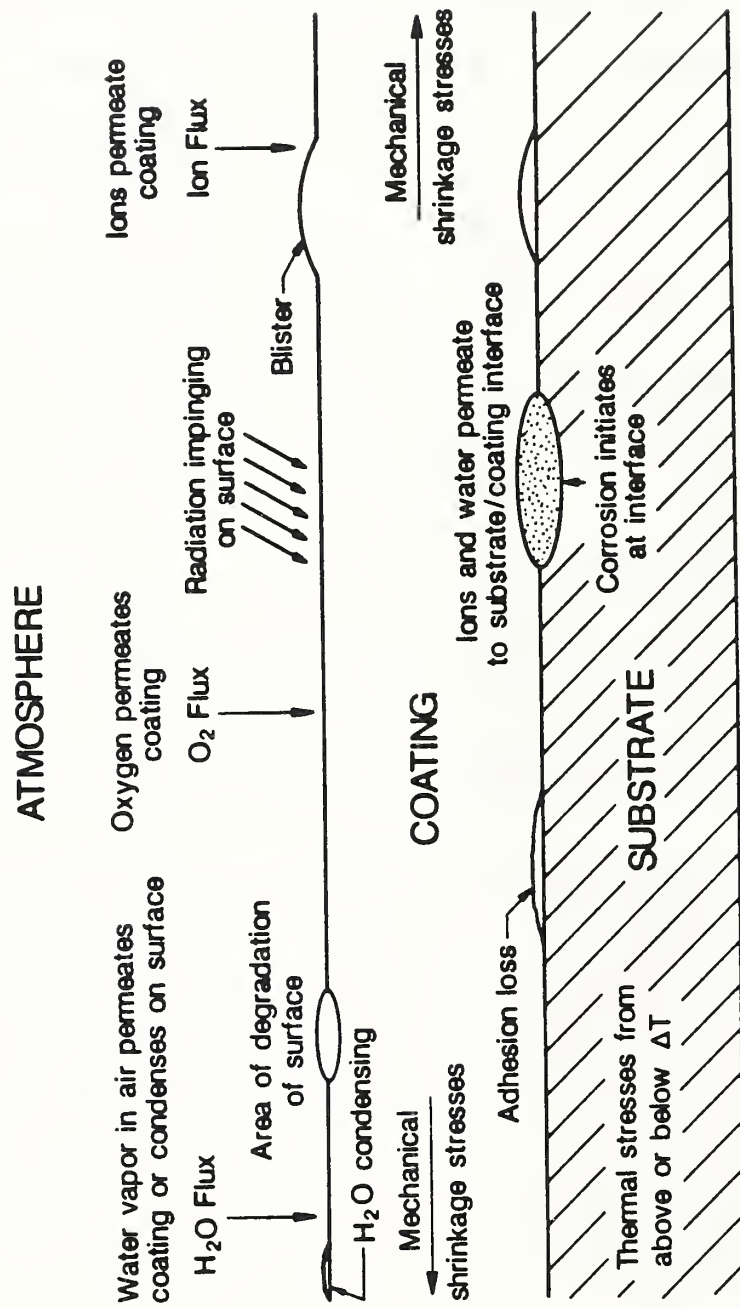


Figure 4. Schematic diagram of degradation events in a coating.

Factors that affect the service life of a coating system are many, and the interrelationship of some of these factors are presented in figure 5 [Blakey, 1985]. From the illustration in figure 5, it can be seen that the failure of a coating system occurs in the bulk and interfacial region as well as on the surface. Indeed for many applications the failure of a coating system occurs at the coating/substrate interface. In an attempt to define durability by a numerical quantity, Bierwagen [1987] separated some of these factors into independent variables (those that affect durability) and dependent variables (measure of durability). Unfortunately, he completely ignored variables other than those of the coatings and the environments. Figure 5 shows that not only the coating materials and environmental factors, which are very complex by themselves, but also the substrate, substrate surface properties and coating/substrate interface play important roles in the service life of a coating system.

4.2 ASSESSMENT OF RELATIONSHIP BETWEEN APPEARANCE AND PROTECTIVE SERVICE LIVES

It is true that gloss loss and other surface appearance changes, such as fading and yellowing, are related to the degradation of the resin as discussed above. Similarly, as a coating degrades it becomes oxidized, rougher or more porous leading to a decrease of the contact angle. However, as Kaempf, et al. [1974] indicated, both gloss and chalking tests indicate only the number of pigment particles exposed per unit area of the coating surface but do not indicate the depth of the degradation of the coating film. This means that chalking, gloss measurements, contact angle and weight loss results may yield different and incomparable conclusions about the weather resistance of a coating.

For a typical coating system, which consists of a coating, a substrate and in between a coating/substrate interface, degradation does not always manifest itself at the surface [Croll, 1987]. For example, a new paint on a car may start to peel before any sign of degradation on the surface as a result of driving through salted roads a few times; or a new paint on a building may start to blister or flake off before any surface degradation is apparent.

Starting with the substrate itself, it is well known that painted alloy steels are more resistant to corrosion than pure steel. Similarly, an epoxy coating on an untreated, low surface energy substrate, such as polyethylene, probably will have a very short service because of poor adhesion. Additionally, the substrate surface properties, such as the surface chemical composition, surface profile, concentration of contaminants, etc. play a major role in determining the service life of a coating system. It has

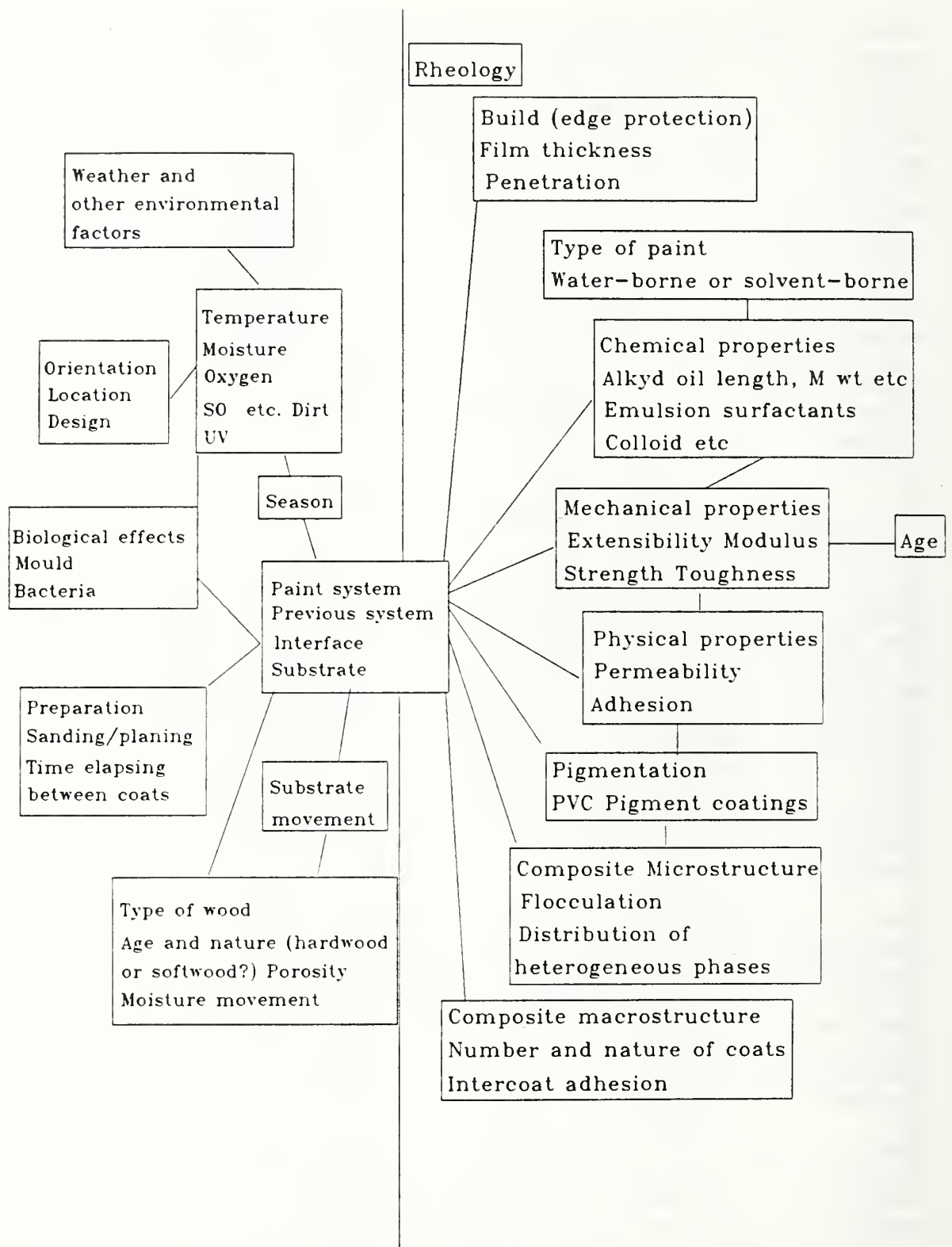


Figure 5. Factors influencing the durability of a paint system [Blakey, 1985].

been generally recognized that proper surface preparation, resulting in a fresh and clean surface, is essential for long term durability of protective coatings on metals [Appleman, 1987], wood [Feist and Hon, 1984] and other substrates. For example, Underhaug et al., [1983] indicated that correct surface preparation of the wood is essential for the durability of the painted structure. Indeed, it was shown that at least 1 mm of weathered wood surface must be removed if the performance of the applied coatings was not to be adversely affected. A superficial sanding may not be adequate to ensure satisfactory performance. Similarly, a paint applied on a greased or dirty surface will also peel off in a relatively short period of time [Hess, 1979 p. 203]. Coating/substrate interface properties, such as adhesion, and the mechanism by which the binder attaches (physical attachment or chemical reaction) and orients on the substrates also play an important role in determining the failure mechanism, such as blistering, flaking, delamination corrosion, etc., [Adhesion Aspects of Polymeric Coatings, K.L Mittal, Plenum Press, NY, 1981] of the coating system. The above examples indicate that substrate, substrate surface and coating/substrate interface properties are important factors in determining the service life of a protective coating system. Yet, these factors have very little, if any, effect on surface degradation or on appearance change of a coating system during service.

Probably the most convincing evidence that the service life of a protective coating system often is not related to appearance change and degradation of the coating surface but is related to failures at the interface is from the wealth of information on corrosion of painted steels and related topics. [Funke, 1978; Dickie and Smith, 1980; Dickie, 1983; Holubka, 1983; Leidhesier, Jr., 1983]. Information obtained by surface analytical and electrochemical methods indicates that the locus of failure of a coating system on steel exposed to a corrosive environment occurs mainly at the coating/steel interface. Corrosive elements, such as water, oxygen, and ions, migrate to the interface and the resulting delamination is due to water or corrosion products formed at the interface with little evidence of degradation on the surface of the coating. This type of failure is accelerated by an applied potential or the presence of a defect in the coating, again emphasizing the fact that the degradation of a coating system exposed to a corrosive environment does not necessarily involve surface degradation but rather the phenomena occurring at the coating/substrate interface. Research at the National Bureau of Standards also showed that an epoxy film on steel delaminated after only 100 hours of exposure to 82% RH and 40°C, while observable chemical degradation of the coating at the interface occurred only after months of exposure [Nguyen and Byrd, 1986].

Furthermore, the use of conversion coatings, corrosion inhibitors, adhesion promoters, physical and chemical surface

treatments of metals and plastics, to name a few, before painting, are evidence indicating that phenomena occurring at the coating/substrate interfacial region during service account for the major mechanism of failure leading to loss of film durability. This is in contrast to the failure mechanism associated with surface degradation and appearance change.

5. CONCLUSION

Surface appearance change, such as gloss, is a valuable tool to monitor the appearance durability of decorative coatings and appears to be a useful tool for the evaluation of maintenance cycles for glossy coating systems exposed to environments where the degradation occurs monotonically and mainly on the surface of the coating. However, the examples and information presented strongly indicate that the use of surface degradation of a coating and, hence, surface appearance changes, is not a suitable criterion for assessing the protective function of a coating system. In many environments, degradation of the interface and bulk takes place in addition to degradation of the surface of the coating. In such environments, not only the coating and the environmental factors, but the substrate, substrate surface properties and phenomena occurring at the coating/substrate interface are the controlling factors that determine the durability or failure mechanisms of a coating system. Indeed, Leidheiser [1983] stated in reference to a particular failure of a coating applied to metal, "The fault does not lie in a special domain--it is a fault of the system, i.e., the metal/pretreatment/coating/application method. The major improvements in coatings will arise when the manufacturer, the assembler, and the user think in terms of coating systems."

Testing procedures to predict the service life of coating systems await developments in several areas including 1) improved understanding of the mechanisms of degradation, 2) improved understanding of the relationships between environmental factors, coating system properties and system degradation, 3) improved characterization of key factors causing degradation and material properties that effectively indicate system performance, and 4) improved mathematical models to predict system behavior in specific environments. To obtain this information, major improvements in the questions being addressed and design of experiments to address the specific questions are required.

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Appendix: PRINCIPLES OF APPEARANCE MEASUREMENTS

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1. INTRODUCTION

The measurable attributes of appearance of a coating can be divided into two broad, but not completely independent, categories: chromatic (ie., having to do with color) and geometric (i.e., having to do with gloss, haze, etc.). Although it is beyond the scope of this report to present a detailed discussion of color theory and principles and the scientific basis for other appearance measurements, a basic knowledge of color and colorimetry, as well as factors that affect other appearance measurements such as gloss, is needed to understand appearance measurements parameters and changes discussed in the report. Detailed discussions are available in many references (e.g., Hunter, 1987; Wyszecki and Stiles, 1982; Billmeyer, 1981). Hence, basic appearance theory and principles and methods of measuring appearance properties are summarized in this appendix.

2. COLOR MEASUREMENT

2.1 VISUAL CAPABILITIES

The color appearance of an object depends on the following three primary variables:

1. The visual sensitivity of the observer (detector) at the moment that the object is viewed;
2. The spectral reflectance distribution of the object which depends on the particular pigments (or dyes) that give the object its characteristic color;
3. The type of illumination, including daylight, under which the object is viewed.

Human visual sensitivity is mediated by two types of photoreceptors: the rods, sensitive to light and operational at relatively low light levels; and the cones, sensitive to color and color differences, and operational at relatively higher light levels. The cone system consists of three photoreceptors types with photopigments whose maximal sensitivities occur at about 450nm (blue), 530nm (green), and 560nm (red) (Hurvich, 1981). Although these visual sensitivities can vary between individuals, particularly for those people termed "color defective," the scientific basis for the measurement of color is the existence of these three different color-response mechanisms in the human eye.

2.2 SPECIFICATION OF COLOR APPEARANCE

For a color to have the correct appearance, the light source for the color must contain light of the appropriate wavelengths. Thus, a red surface appears red because it selectively absorbs

wavelengths other than red, and it reflects more of the long wavelengths (i.e. red) than of those in the middle or short wavelength end of the visible spectrum. Sources, surfaces, and media that are not differentially selective in the wavelengths they send, reflect, or transmit to the eye are seen as "achromatic" rather than color. They appear black, gray or white. Note, however, that the red object cannot preferentially reflect long wavelengths if no long wavelengths are supplied by the light sources being used. The worst type of light source for lighting colors correctly is a monochromatic one (containing one wavelength). No object, whatever its reflectance spectrum, can send light that is not in the illuminant's spectral power distribution to a color receptor, human or machine. As a result, monochromatic light drastically alters the appearance of a colored object compared with "white" light. In other words, the monochromatic source has poor "color rendering." Color Rendering is defined as a "general expression for the effect of a light source on the color appearance of objects in conscious or subconscious comparison with their color appearance under a reference light source." (IESNA, 1984, p. I-8). The Color Rendering Index (CRI) provides a "measure of the degree of color shift objects undergo when illuminated by the light source as compared with the color of those same objects when illuminated by a reference source of comparable color temperature" (IESNA, 1984, p. I-8).

The first two factors to be considered in defining color appearance, then, are the visual sensitivities of the observer or receptor, and the spectral characteristics of the light source. The third factor, which will be discussed at length in the present document, is the reflectance spectrum of the object itself. Color scales grew out of experiments that determined the specific way human observers respond to spectral distributions of light. (See Hunter, (1987) for a complete discussion of standard color observers, development of the 1931 CIE color space, color matching experiments and color spacing experiments.) Numerous systems or scales have been used to define the "color" of an object, beginning with simple nomenclature such as "red", "green", "blue", etc.

Specification of exactly what is meant when one gives a name such as "red" to an object is not easily done, however. Does one mean "red", "magenta", "burgundy", or what? The challenge is to specify the desired "red" so that another person can recognize and reproduce, if necessary, the desired color. Toward this end, a number of systems with varying degrees of specificity have been developed. These include the Munsell color order system, the ISCC-NBS color name system, the CIE chromaticity coordinate system, and others.

The Munsell color system is a system of surface color specification based on perceptually uniform color scales for

three variables hue (or nominal color), value (lightness), and chroma (saturation). It is often represented by a physical set of more than 1500 color chips which are organized into a three-dimensional color solid which represents the color's hue, value (or lightness) and chroma (or saturation). Hurvich (1981, p. 275) describes the system this way: "The individual chips are ordered into a three-dimensional color solid with a vertical black-to-white axis. HUES are arranged in equal angular spacing around the central axis, and CHROMA (saturation) is the distance of a chip from the central axis at any given VALUE (lightness) level." There are five principal and five intermediate steps to the hue circle, which is arranged from 5R through YR, Y, GY, G, BG, B, PB, P, RP and back again to red. There are ten steps from black to white for the value scale, and up to sixteen steps from neutral to highly saturated for the chroma scale. Although differences between the individual color chips are intended to be equal, it is known that they are not in all cases. The specifications for a particular Munsell color are given by three sets of alphanumeric characters which define its hue, value, and chroma. Thus, a red color might be represented as 7.5R 4/14 meaning that it has a red hue which is intermediate between 5R and 10R, a value of 4, and a chroma of 14 (which is very saturated). The Munsell system allows one to match colors to it under a specified illuminant; it does not allow one to predict how the color might appear under a different illuminant. One also needs a copy of the Munsell Book of Color, or its equivalent, to actually make the match. Familiarity with the Munsell system is essential when making accurate specifications of colors.

Another color order system, also based on perceived differences between colors, is the Swedish Natural Color System (NCS). In this system, color is expressed in terms of six elementary properties which relate to the way in which the human visual system operates. These properties include white, black, yellow, red, blue, and green, and represent the six color sensations that are unique (Hunter, 1987). A color atlas has been prepared that provides a visual illustration of the NCS notational system, using 1412 colors. Neither the notational system nor the atlas has found widespread acceptance in the U.S. as yet, even though provisions are made for translating into the CIE system.

The ISCC-NBS system is yet another system for naming colors. This system attempts to use familiar color names so that less training is required to use it. Kelly and Judd (1976) developed to set up a Universal Color Language (UCL) which includes both the ISCC-NBS color naming system and the Munsell notation system. They indicate that the Universal Color Language is intended to be "a method or language of designating colors in simple, easily understood but accurately defined color designations in definite, correlated levels of accuracy of color designation" (p. A-18). The UCL contains six levels of increasing color specification

accuracy. At each level, the color solid is divided into specified numbers of color blocks; the boundaries for each block are defined; and each level is related to all other levels. At level one, colors are specified in terms of 13 common color names, such as red, yellow, green, etc. These 13 blocks are further subdivided into 29 blocks for level 2. Level 3 contains the ISCC-NBS system of designating colors, using a full set of 267 color names. Billmeyer and Saltzman (1981) indicate that level three allows the use of modifiers, which adds words related to value and chroma. Level 4 is divided into 1500 blocks corresponding directly to the Munsell system. In level 5, the Munsell system is subdivided still further by visual interpolation between color blocks. Finally, in level 6, color can be measured instrumentally and specified numerically by the CIE chromaticity coordinate system. The Universal Color Language thus provides a way of specifying color appearance from simple naming to detailed instrumental measurement. It should be noted that the UCL is intended to be applied to colors seen under average daylight, as represented by the CIE standard source C.

A third system for specifying, and measuring, object color is the CIE Chromaticity system. The CIE system relies on the idea that color appearance results from the combination of the light source, observer response, and object reflectance. For use in the system, the CIE recommends a series of standard light sources, with CIE Sources A, C, and D_{65} being the most commonly used ones. It also recommends two Standard Observers with representative (normal) color vision.

The CIE system is based on the principle that three fixed colored lights (or "primaries") can be mixed to match any color (by means of a colorimeter or other instrument). The three primaries needed to match the specified color are termed tristimulus values. These are derived from color matching data collected on a large number of observers by the CIE in 1931. To avoid variations in observer matches, the CIE specified a Standard Observer based on the average value of the 1931 color matching data for a 2° field (Wyszecki and Stiles, 1967) and another Standard Observer in 1964 for a 10° field.

The CIE system is defined by three functions of wavelength, \bar{x} , \bar{y} and \bar{z} which represent the tristimulus values of the single wavelengths of the spectrum. (Although the tristimulus values could be red, green, and blue, corresponding to human receptor sensitivities, this would require the use of negative numbers for the mathematical calculations. As a result, in 1931, the primaries of the CIE system were chosen in such a way that these spectral tristimulus values are all-positive functions. Different choices for the primaries could result in negative values.) It follows then that "To specify any illuminated object or surface colorimetrically we only require the object's or surface's spectral reflectance or transmittance and the spectral

energy distribution (in relative terms) of the light source illuminating it. If the products of these two distributions curves at each wavelength are then multiplied by each of the standard observer spectral tristimulus values at each wavelength and the resultant values for all wavelengths added separately, we obtain the three numbers needed to specify the color. These three summed values are called the X, Y, and Z tristimulus values," Hurvich (1981, p. 284).

The CIE defines "chromaticity" as the "color quality of an object defined by its chromaticity coordinates. "The chromaticity coordinates x , y , and z are fractional equivalents of X , Y , and Z ; i.e., $x = X/(X+Y+Z)$, etc. Because the CIE chromaticity coordinates are fractions whose sum is unity, if two coordinate values are known, the third can be derived arithmetically. This principle has been used to develop the CIE chromaticity diagram, which is a two-dimensional diagram upon which the x and y coordinates are plotted. ASTM E 308 - 85 defines the tristimulus values as "the amounts of the three CIE stimuli which, for the specified observer, illuminant, and geometry of illumination and view, define the psychophysical color. The colors of two specimens 1 and 2 will match under the specified conditions when their respective tristimulus values are equal" (p. 167). Figure 1 provides a diagram of the CIE chromaticity system with standard illuminant D_{65} . The outer line which resembles a horseshoe contains points which represent lights of a single wavelength. This line is termed the spectrum locus. The line that forms the bottom edge of the horseshoe is termed the "line of purples". In the center of the diagram are located white colors, such as $x = 0.310$, $y = 0.317$ or CIE Illuminant C. The CIE diagram is used to plot the chromaticity of an object without reference to a set of color chips or standard colors. On this diagram, a red might be plotted as 0.596, 0.327 for example.

Through the years, a goal of color specification systems is that differences between colors be equal - a principle that is violated in the CIE chromaticity system. The CIE has made several attempts to improve the spacing in the system by use of different mathematical transformations. These include the Uniform Chromaticity Scale, or UCS, the CIE u, v system, the CIE u', v' system, and finally the CIE $L^*a^*b^*$ (or CIELAB) system. The CIELAB system, which has become widely used for color specifications, is based on the idea of an opponent color space in which red-green form one dimension, yellow-blue another, and black-white a third. These dimensions correspond to human color perception in which reddish greens and bluish yellows do not occur. In the CIELAB system, "a" represents the red-green dimension, with positive values being red, and negative values being green. Similarly, "b" represents the yellow-blue dimension, with positive values being yellow, and negative values being blue. Finally, "L" represents a lightness (or black-white)

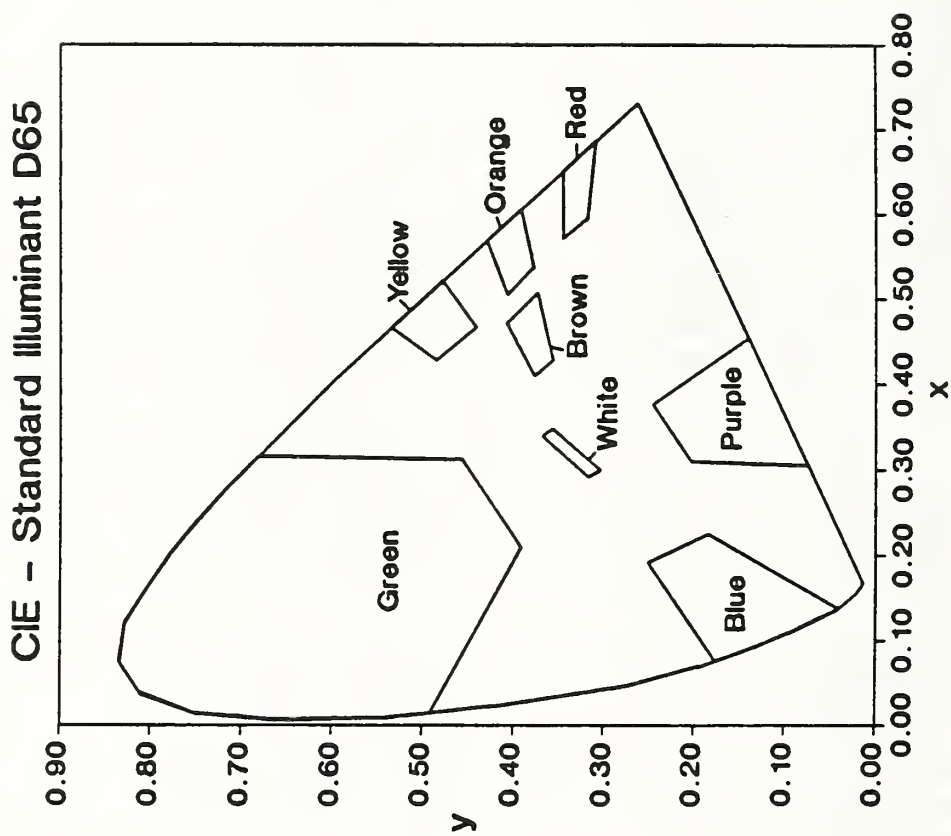


Figure A - 1. Diagram for the CIE chromaticity system under D_{65} .

dimension. In this system, our red might plot as $a^* = 55.32$, $b^* = 38.87$ and $L^* = 42.2$ for Illuminant C.

Another less widely used system is the CIELUV system. This system is most useful for specifying the color of lights. Billmeyer and Saltzman (1981, p. 104) comment that those "who prefer a color space that has a chromaticity diagram, that is, a linear transformation of the CIE x,y diagram, will prefer the CIELUV space and probably wish to use the corresponding color-difference equation. Those dealing with the use of colorants in paints, plastics, textiles, and the like, and who may be familiar with the Adams-Nickerson equation, will probably prefer to use CIELAB." Robertson (1977) found that the Munsell loci of constant hue and chroma were represented slightly more accurately in CIELAB. Many of the measuring instruments now provide readings in CIELAB, as well.

Another system in which a serious attempt was made to provide even perceptual spacing between colors is the OSA system of Uniform Color Scales. This system consists of 558 colors spaced according to three dimensions: blue-yellow, red-green, and black-white. Each sample has 12 neighbors, each of which is equally distant in color from the central color. Attempt are being made to translate this system into a mathematical system for instrument specification with the ASTM E-12 Committee on Color Appearance currently developing a standard practice for specifying color with the OSA scales.

2.3 COLOR CHARACTERIZATION USING COMPUTER IMAGE PROCESSING

The major color specification systems used in color science today have been reviewed in the preceding section. There are other systems, among them the Pantone and Ostwald systems, primarily used for printing and ink specifications. These systems lack the translation into instrument measurement systems that characterizes the CIE systems, however.

A new procedure for characterizing color is based on color video image acquisition and image processing. The image sensor used is usually a charge-coupled device (CCD). A CCD is a monolithic silicon integrated circuit. Packets of electronic charges are moved by electrostatic potentials controlled by clock signals applied to gate structures. CCD line scanning image sensors contained in color cameras are monolithic structures containing rows of image sensing pixels, transport registers and an output amplifier. Light energy striking the CCD surface generates free electrons which are accumulated as charge packets within the pixels. The architecture for a typical high-performance, low noise CCD is listed below. Color can be described electronically in terms of the red, green and blue (RGB) components.

CCD Image Sensor Architecture

<u>Element</u>	<u>Value</u>
Pixel elements	510H x 492V
Video format	17 mm
Pixel size	13 mm(V) x 17 mm(H)
Spectral response	Visible spectrum
Clock frequency	9.545 MHz

The equipment and procedures used to characterize color using color image processing are discussed below.

2.4 MEASUREMENT TECHNIQUES

2.4.1 Perceptual

The simplest color measurement technique is the visual match in which the target or specimen color is directly matched against a standard color. Examples include the Munsell Book of Colors and the Highway Color Tolerance charts. In each case the specimen is matched against a standard. The Color Tolerance Charts (FHWA, 1965) provide a set of colors, including a standard safety color, and six limit colors. The limit colors differ in hue, value, and chroma. A user would match a highway sign color using the chart under "North Daylight or scientific daylight having a color temperature of from 6500° to 7500° [K]". Sign color should not deviate past these limits. The assumption is made that the user has normal color vision and is using proper lighting geometry; namely that the color is illuminated at 90° and viewed at 45°. The normal color vision assumption breaks down for the 8 to 10 percent of the male population who have either anomalous or missing photopigments, however.

The ability to match colors accurately also requires that one use the same light source used in the original match. The reason for failures in matches as light source is changed is termed metamerism. It means that samples which match under one light source may not match under another source. The reason is that they do not have the same spectral reflectance curves, even though they may have the same CIE chromaticity coordinates (Billmeyer and Saltzman, 1981). Billmeyer and Saltzman (1981, p.22) provide the following definition: "We define a pair of objects having different spectral reflectance curves but the same color coordinates for one set of conditions as metameric objects, or a metameric pair. They are said to exhibit metamerism. Pairs of objects having the same spectral reflectance curve and, therefore, the same color coordinates for all sources, are non-metameric and form an invariant pair." Object metamerism occurs because different colorants (dyes, pigments) with different

spectral characteristics are used in samples to be matched (ASTM D 4086 - 82). Observer metamerism, in which two observers (or instruments) have minor (non-color deficient) differences in the spectral response curves of their visual photopigments, can also occur. For these reasons, then, the success of color matches depends on the use of known lighting and observer conditions.

Two ASTM committees, D-1 on Paint and Related Coatings and Materials and E-12 on the Appearance of Materials, have developed standard practices and test methods for evaluating the color and other appearance attributes of objects. Recently the E-12 committee compiled the various standards into a single volume entitled "ASTM Standards on Color and Appearance Measurement" (1987). This volume is an invaluable compendium of all relevant standards on appearance measurement. Key points from various standards will be summarized in the following pages.

ASTM D 1535 - 80 provides a method for specifying colors visually in terms of the Munsell system. The specimen should be placed on a neutral (white or medium gray) background and illuminated with daylight (natural or artificial) at an angle of 45° above horizontal. Using the Munsell Book of Color, the specimen is matched for value, chroma, and hue in that order by selecting the constant hue charts or chips immediately adjacent to the hue of the specimen. A gray mask should be used so that only the specimen and one chip can be seen at a time. The value of the specimen is determined first by finding chips whose value is on either side of that of the specimen. Value is estimated to the nearest tenth of the interval between adjacent value steps. To determine chroma, one selects chips of the same value of the sample, and estimates their chroma to the nearest fifth of the two-chroma interval between chips. Finally, one determines hue by interpolating between chips of nearest value and hue in the charts and estimating to the nearest fifth of the 2.5 hue-steps between hues. The standard notes that the precision of the visual comparison is 0.5 hue step, 0.1 value step, and 0.4 chroma step. Of course the Munsell notation can also be determined by mathematical translation from the CIE system.

ASTM D 1729 - 82 provides procedures for visually determining color differences for opaque materials, without reference to color charts such as the Munsell charts. It specifies the spectral, photometric, and geometric conditions under which reasonable color difference judgments may be made. Three different light sources are specified - artificial daylight approximating D_{65} , incandescent with a color temperature of 2300 $^\circ\text{K}$, and a minus-red source (such as cool white fluorescent with a correlated color temperature of 4400 $^\circ\text{K}$). Four different illuminances are recommended: 100 to 125 fc (1080 to 1340 lux) for critical evaluation of materials of medium lightness; 75 to 175 fc (810 to 1880 lux) for general evaluation of intermediate lightness materials; 50 fc (540 lux) for general or critical

evaluation of very light materials; and as much as 200 fc (2150 lux) for very dark materials. As far as geometry is concerned, the lighting should be overhead using an extended source with uniform ($\pm 20\%$) illumination. Ideally the evaluation area should be shielded from extraneous light using permanent non-glossy (15 on a 60 degree scale of gloss) structures of specified Munsell hue (N6 to N7) and chroma (0.2 to 0.3). For glossy specimens, a black matte surface (such as velvet) should be placed on the wall opposite the observer to minimize reflections. Similarly, the observer must guard against reflections from the overhead light source by viewing specimens at approximately 45° from perpendicular. If the light source is ahead of the observer (as in a light box), this may also require tilting the specimens away from an observer at an angle of $8-9^\circ$ from the horizontal. Differences between specimens in hue, lightness, and saturation should be noted, although no instructions for using the Munsell system are given explicitly in the standard. It is left up to the observer to determine if the two samples differ, and whether the difference is acceptable.

Another ASTM standard, D 2616 - 67, provides for visually determining differences in color by using a gray scale. This standard makes the assumption that a color difference between opaque specimens can be determined by use of a gray scale. The gray scale is made up of Munsell neutral gray chips paired with lighter Munsell gray chips to form nine steps of contrast or color difference, ranging from a Munsell value difference of 0 to one of 1.23. (A difference in Munsell value of 0.1 corresponds to about one CIELAB unit of difference.) The difference between the colored specimens can then be matched with the difference between the two Munsell grays. The result is a summary measure of the overall difference in value, hue, and chroma between the specimens. Information about differences in each dimension is not provided. The accuracy of the differences between samples is related to the uniformity of the specimens (with non-uniform samples having smaller differences than uniform) and to the sharpness of the dividing line between samples (with sharply divided samples having a greater difference). ASTM D 2616 recommends that only personnel with normal color vision, preferably those testing in the superior range with the Farnsworth-Munsell color vision test, should be used. Daylight conditions, such as those recommended by D 1729, should be used at least 100 fc (1076 lux). The standard recommends close proximity for the samples and the gray scale, but says that distances of 1 in. (25.4 mm) or more may be used. It also recommends that a gray mask be used so that areas of the specimen to be measured are equivalent in size to those in the gray scale. Finally, the standard cautions that reliable test results require "use of the specified surround and angles of illumination and viewing, equivalent gloss and texture of pairs under examination, and identical weighting of the three attributes of hue, lightness, and saturation" (p.93), as well as observers with good

color vision and use of good lighting. The standard indicates that repeatable measures within a Munsell value difference of 0.15 are possible.

ASTM D 4086 - 82 on Visual Evaluation of Metamerism is the final ASTM standard to be discussed here on visual evaluation of colors. It provides visual methods for detecting that two samples are metameric (have different spectral reflectance distributions), and for estimating the amount of metamerism. Very simply, the practice recommends that the observer determine that two specimens match under one light source and then rematch them under one or more light sources with noticeably different spectral power distributions. Thus if the first match is made under incandescent light, the second should be made under daylight or cool white light. The greater the difference between light sources, the greater the likelihood that small metameric differences will be seen. The degree of metameric difference can be estimated by using the gray scale pairs specified in D 2616. ASTM D 4086 notes that visual inspection of the spectral reflectance curves can also be used to determine if two specimens are metameric. If the curves intersect three or more times, then the specimens are metameric. Judgement of the degree of metamerism from visual inspection of the curves is not easy and requires considerable experience, however.

2.4.2 Instrumental

None of the visual methods for determining color changes, differences, or metamerisms provide predictive, mathematical information about the likely extent of variation between two colored samples. For this sort of information a number of instrumental techniques, based on the CIE system have been developed. In addition, many studies [e.g., Cheung and Rigg, 1986 and Witt, 1987] and a review [McDonald, 1982] have been carried out to further the understanding of the relationship between visual and instrumental assessment of color differences. Wyszecki and Stiles (1982) defined three types of colorimetric measuring instruments: the spectroradiometer, the spectrophotometer, and the tristimulus-filter colorimeter.

Wyszecki and Stiles (1982, p. 229) note that a spectroradiometer is "designed to measure radiometric quantities as a function of wavelength", at intervals as small as 2 nm. To oversimplify, a spectroradiometer contains a monochromator and detector for measuring the radiant power of a test source. It may also emit a reference source of known spectral power distribution. If configured properly with a perfect diffuser, it can be used for colorimetric purposes, although both the spectrophotometer and colorimeter are more traditionally used in this application.

Wyszecki and Stiles (1982) note that a spectrophotometer is similar in design to a spectroradiometer. Its objective is

different, however; namely, to compare the radiant power leaving an object at each wavelength interval with the power incident upon it and thus obtain the spectral reflectance (transmittance) factor of the object. Billmeyer and Saltzman (1981) define spectrophotometry as the measurement of the spectral reflectance (transmission) curves of objects or materials. They note that the instrumentation requires a source, monochromator (means of providing monochromatic light of 0.1 to 10.0 nm) and a detector. The sample is illuminated by a small portion of the visible spectrum and its reflectance at those wavelengths is measured. The procedure is repeated throughout the spectrum. Samples may be measured with bidirectional geometry in which the sample is illuminated at 45° from the normal and measured along the normal (or the reverse geometry); or they may be measured in an integrating sphere which collects all the light reflected from the sample. Use of an integrating sphere is the best procedure for measuring haze and translucent samples (Billmeyer and Saltzman, 1981). The source must be stable and contain sufficient power at each wavelength to allow the instrument to measure the reflectance of the sample. The data obtained, however, are independent of the source.

ASTM E 284 defines a colorimeter (or a tristimulus colorimeter) as an "instrument that measures color, in terms of tristimulus values, often by the use of filters to convert the relative spectral power distribution of the illuminating source to that of a standard illuminant, and to convert the relative spectral sensitivity of the sensor to sensitivities prescribed for a standard observer". Billmeyer and Saltzman (1981) note that a colorimeter uses only three or four colored lights (unlike the modern spectrophotometer) as illuminants. The intent is that the combination of filters and illuminant "equal that of the combination of one of the CIE standard illuminants (usually illuminant C) and the tristimulus values of the spectrum" (Billmeyer and Saltzman, 1981, p. 85). Thus the instrument readings should approximate the CIE tristimulus values through use of colored filters as "an optical analogue of the numerical data used to obtain CIE coordinates from spectrophotometric data" (Billmeyer and Saltzman, 1981, p. 85). Wyszecki and Stiles (1982) comment that "a tristimulus filter colorimeter is an instrument with spectral response functions directly proportional to the color-matching functions of one or the other CIE standard colorimetric observers. Its importance as a tool for production control of colored objects is well established. Most commercially available instruments of this kind are satisfactorily precise and easy to operate, and they are fast enough to measure many specimens a day. However, many of them lack accuracy; that is, tristimulus values read by such instruments do not generally agree with tristimulus values obtained by spectrophotometry and computation." (p. 243) The instrument is useful, nonetheless, in numerous practical

applications requiring precision but not absolute accuracy, including colorimetry by differences (Wyszecki and Stiles, 1982).

2.4.3 Color Video

Recent advances in the development of computer image processing hardware and the evolution of the personal computer have resulted in low cost computer image processing capabilities. For example, a leading manufacturer of a state-of-the-art color image processing system has reduced the price of its entry level system by 75% (from \$100k to \$25k) during the past year. The industry trend in the design and production of digital image processing hardware is to target the devices for workstation configurations. Also, new techniques and devices are being introduced to improve the image acquisition part of image processing. Figure A-1 presents two color image processing system configurations. Still, there are many considerations in the selection of a coherent image processing system, since most systems for scientific use require special features such as high image resolution, filtering, and relatively large CPU processing requirements. This brief overview presents representative equipment configurations and capabilities which relate to the acquisition and processing of color images for materials science.

2.4.3.1 Color Image Acquisition Devices

High performance color cameras for image acquisition are Charged Coupled Devices (CCD). An important consideration in the selection of the camera is the number of scan lines. The scanning range found in most cameras manufactured today is between 200 and 625 lines. One attempts to match the maximum number of scan lines with the desired quality of the image. The more scan lines, the better the quality. In addition to scan lines, the resolution of the camera is determined by a given number of comparable TV lines. Higher resolution cameras will provide between 300 and 400 lines in the horizontal and vertical direction. The scanning resolution translates into an effective pixel resolution for the image. As is obvious, color cameras provide reduced resolution when compared to their monochrome counterparts, some monochromes having as high as 1280 by 1024 resolution.

There are several standard signals used in video devices today. The following table identifies these signals and their definition. The NTSC signal provides the color data necessary to acquire color images.

Figure A-2: Color Image Processing System Configurations

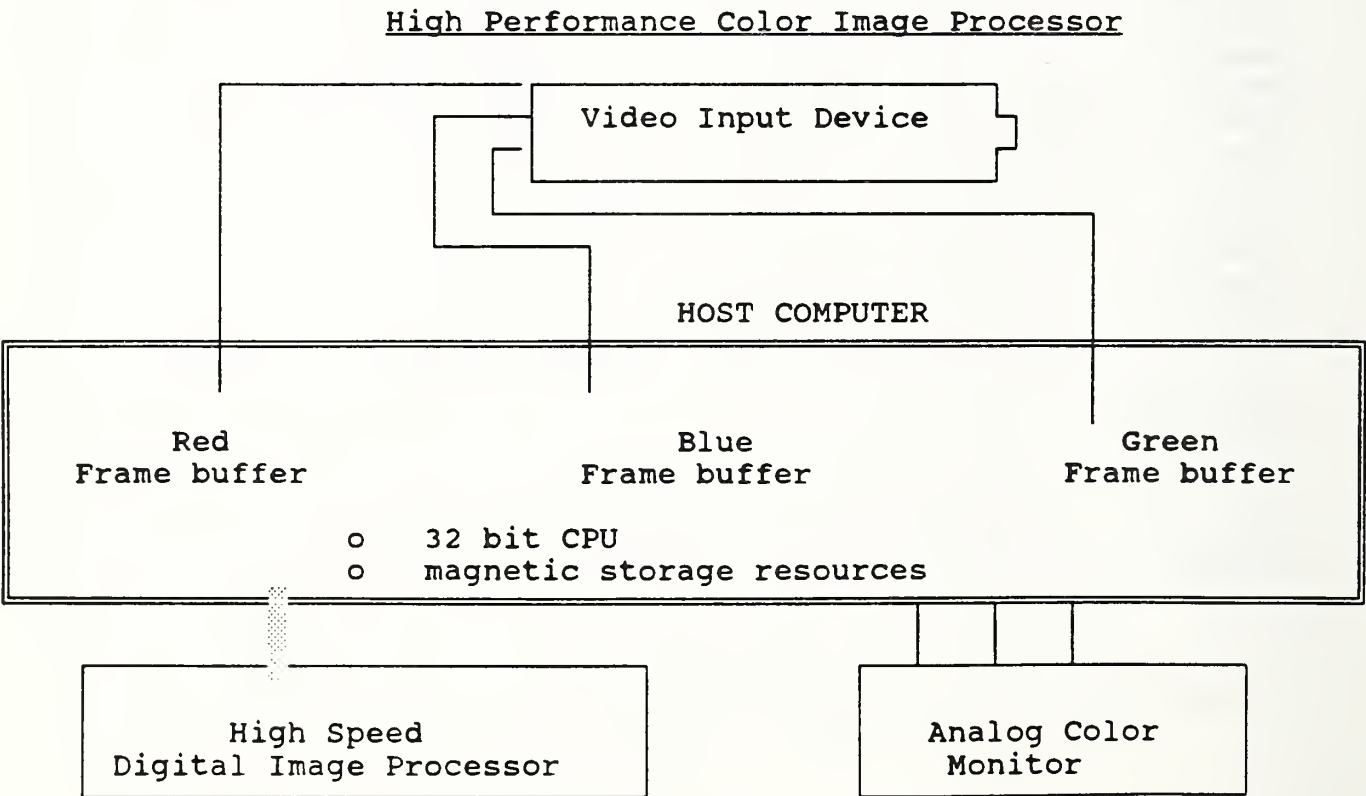
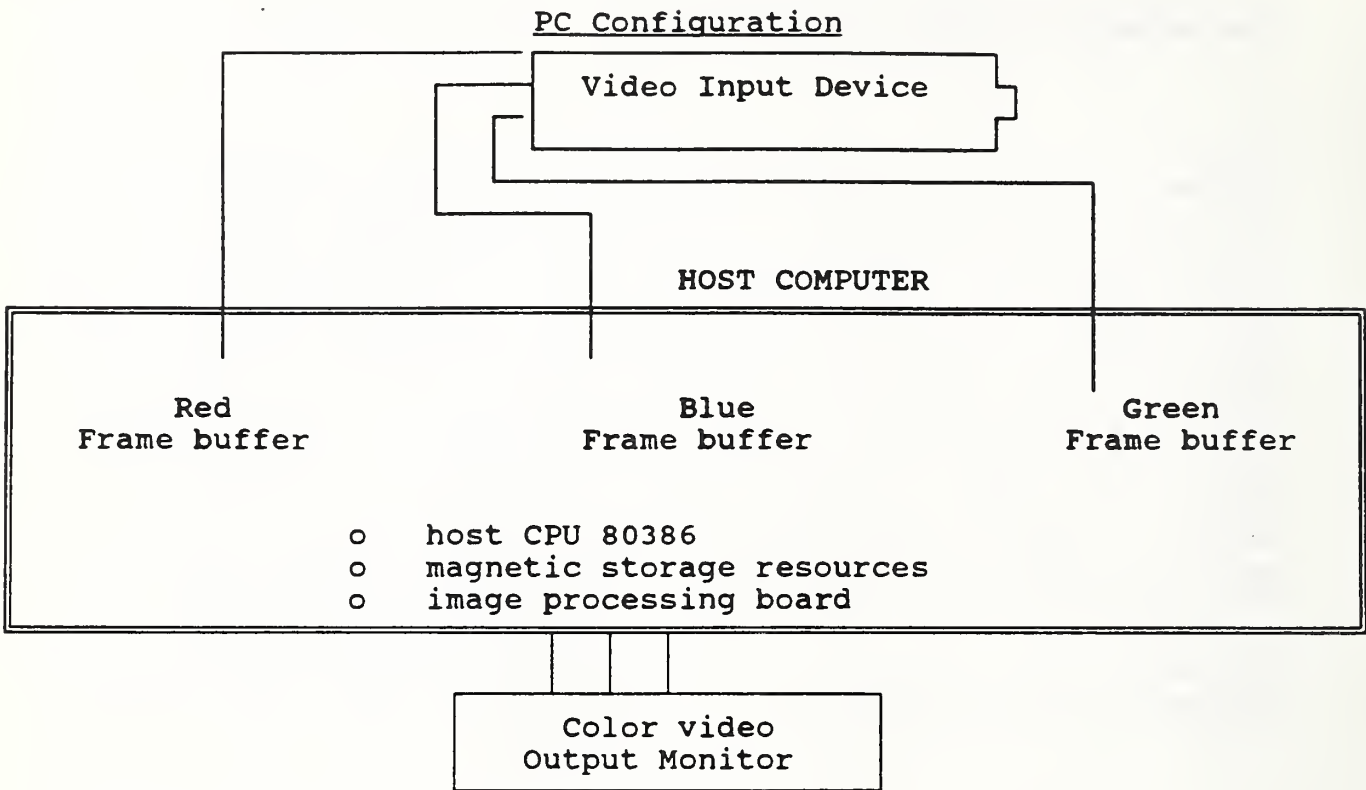


Table A-1: Video Device Signals

<u>Signal</u>	<u>Use</u>
RS-170	monochrome and sync timing data
NTSC (National Television System Committee)	same as RS-170 plus color data (60-Hz)
PAL (Phase alternation-line)	50-Hz television systems
CCIR (Intl. Radio Consultative Committee)	50-Hz television systems

2.4.3.2 VCR Input Devices

Historically, VCR devices have not provided high quality image acquisition. Since VCR output signals are NTSC, the color information in the signal degrades image clarity, and is often misinterpreted as an interference pattern. Newer frame-grabber designs overcome these obstacles through the use of color filters and advanced circuits. This is an important factor in matching the VCR device to the frame-grabber.

2.4.3.3 Frame-Grabber Devices

Color images are acquired from the video input device using a device known as a frame-grabber or frame buffer. This device captures the image in addition to conditioning the signal (e.g. filtering). Three frame-grabbers are required for most color image processing applications. Each device is assigned a signal RGB input. Typical resolution of each frame-grabber is 512x512, with 8 bits per color component. RGB color acquisition with three frame-grabbers often requires much fine tuning (synchronization) to achieve the desired image quality. This may be accomplished through software control provided by the frame-grabber manufacturer.

Frame-grabbers are available for a variety of host computers. These range from personal computers to high-performance workstations supporting VME bus protocols to high performance minicomputer systems. The frame-grabber is installed into the bus chassis of the host computer, and serves as the pipeline for supplying image data to the image processing functions of the host computer. The criteria for selecting the host computer is usually determined by assessing the required image processing resources needed to process and store the image. For example,

several megabytes of main computer memory will be required to perform image processing on a 1024x1024 resolution image. Other factors to be considered are disk storage requirements and bus timings which control data transfer within the computer system. For example, careful selection of frame-grabbers for integration into microcomputer systems is required due to the incompatibilities which exist in computer bus speeds.

2.4.3.4 Color Image Processing Capabilities

The processing of color images is performed by an image processing board on a microcomputer based system or by a high performance digital processing subsystem. Characteristics of high performance color image processing systems are; 1) the ability to process images in 2048x2048 pixel resolution; 2) the ability to process image data at CPU speeds of up to 120 million instructions per second; 3) the option for user defined attributes for image definition (e.g. texture maps, 3-D model generations); 4) the ability to represent a pixel in 48 bits of depth. As the industry has matured, image analysis algorithms are maintained in user callable libraries. Previously, these algorithms had to be developed by the user. Menu driven image analysis software can also be found on PC computers.

2.5 MEASUREMENT PROCEDURES

As with the visual evaluation of color samples, ASTM has developed a set of instrumental test methods and procedures, many of which parallel the visual procedures. In one of the most detailed procedures, ASTM E 308 - 85 provides a standard method for computing the colors of objects by using the CIE system. It provides extensive tables and computational procedures for obtaining the tristimulus values from spectral reflectance (or transmittance) data for a given specimen for two standard observers (the CIE 1931 or 2°, and the CIE 1964 or 10° observer).

The Practice assumes that one begins with spectral reflectance measures of a specimen. It gives procedures and tables for determining the CIE tristimulus values from these data. Tables are given for the CIE 1931 and 1964 observers, and for nine standard illuminants, (A, C, D₅₅, D₆₅, D₇₅, F₂, F₇, F₁₁). Source A represents tungsten illumination, Source C and the various D sources represent different types of daylight, F₂ represents cool white fluorescent, F₇ represents broad-band daylight fluorescent at 6500 K, and F₁₁ represents narrow-band white fluorescent at 4000 K. The practice gives calculation procedures for different levels of accuracy using 1nm or 5 nm intervals. To obtain tristimulus values, one selects the desired set of tables for a given Standard Observer and Illuminant. For each wavelength, the tabulated values for the Standard Observer are multiplied by the relative spectral power values for the illuminant and by the reflectance values for the object, and then summed over the range

of 380 to 700 nm for x, y and z and multiplied by a normalization constant to obtain X, Y, and Z. Chromaticity coordinates are then obtained by dividing each tristimulus value (X, Y, and Z) by the sum of all three (X + Y + Z). Many of these computational procedures are built into modern spectrophotometers, so that tedious hand calculation no longer must be done. The practice also gives equations for translating the results into the CIELAB and CIELUV uniform color spaces.

ASTM also provides procedures for calculating color differences between two or more samples, once they have been measured instrumentally. ASTM D 2244-85 provides a method for calculating color differences from instrumentally measured color coordinates and expressing these differences in one of three uniform color spaces. The spaces include the 1976 CIELAB space, the Hunter L_{H} , a_{H} , b_{H} space and the Friele-MacAdam-Chickering (FMC-2) space. ASTM D 2244 defines a computer color difference as "the magnitude and direction of the difference between two psychophysical color stimuli defined by tristimulus values, or by chromaticity coordinates and luminance factor, as computed by means of a specified set of color-difference equations" (p. 86). Differences between two specimens are measured by using a colorimeter or spectrophotometer to determine the tristimulus values for each (in CIE x,y space), and then translating these coordinates into a uniform color space. Color difference magnitudes are then computed from these values.

The rationale for using a uniform color space is to make measured color differences be at least somewhat equivalent to perceived differences through the use of weighting factors. Since there are several different color spaces, color differences obtained for one space such as CIELAB, will not be equivalent to differences obtained for another space such as CIELUV or FMC-2. Use of D 2244 allows a user to determine the magnitude of a color difference as well as the direction of the difference. The standard defines the equations for three color spaces (CIELAB, FMC-2 and Hunter) and explains how to calculate color differences for each one. The standard also reminds the user to select appropriate measuring geometry and to measure at least 3 portions of the specimen to determine uniformity. In addition, it provides information on the desired precision and reliability of color difference measurements made in different laboratories. Minimum acceptable differences range from 0.03 to 0.39 depending on the color space and measuring geometry.

Standard Practice ASTM E 805-81 identifies instrumental methods for measuring colors and color differences of materials. It provides guidance for identifying the samples and specimens, the measuring instrument and lighting geometry, and the reference standard. It also specifies applicable illuminants, standard observers, and color scales.

In E 284-81, ASTM provides a set of definitions of the terms most frequently encountered when describing or specifying the appearance of materials. This list is intended to be the definitive standard for such terms, and as such, forms a valuable reference base for those doing appearance work.

3. MEASUREMENT OF GEOMETRIC APPEARANCE

The ASTM standards discussed thus far provide the basis for color appearance measurement. An equally important area of appearance measurement is that related to the geometry of the object. In the introduction to the compilation of ASTM standards on Color and Appearance Measurement (1987 edition), the editor distinguishes between chromatic and geometric attributes of appearance as well as between physical and psychophysical measurements. (The latter is a measure that correlates both with visual estimates of the appearance of an object and with its physical measures.) The introduction sets up four classes of geometric conditions depending on whether objects reflect or transmit light. The four categories include diffusely reflecting opaque surfaces, specularly reflecting surfaces, translucent (diffusely transmitting) surfaces, and transparent surfaces.

As for color, there are standards for the visual evaluation and instrumental measurements of the geometric properties of objects which will be briefly summarized here. In addition, studies have been conducted to correlate visual determinations of differences in gloss, distinctness-of-image and other geometric properties of coatings with instrumental measurements [Billmeyer and O'Donnell, 1987].

Standard Practice ASTM D 4449-85 covers the visual evaluation of gloss differences using a lamp especially designed for the purpose. It identifies six aspects or types of gloss that one may look for when using the lamp to assess gloss differences between surfaces. These include gloss, specular gloss, reflection haze, distinctness-of-image, texture, sheen and directionality of surface. Differences are rated in four levels from none to considerable.

Standard Practice ASTM E 179-81 provides for the selection of geometric conditions for measurement of reflectance and transmittance of objects. Attributes for which the standard is applicable include color, transmittance, gloss, reflectance, and opacity. The standard cautions that spectral variations are primarily responsible for color appearance, while geometric variations result in gloss, translucency, luster, and similar appearance attributes. Nevertheless, variations in geometry can also affect color, transmittance, and diffuse reflectance. As a result, appearance measurements must specify both the spectral and geometrical characteristics of the measuring situation. The

standard is concerned only with reflection and transmission of light, not with absorption.

Six different types of scale on which a specimen may reflect or transmit light are described in E 179. These include regular, specular, diffuse, total directional and fractional. Regular means only light that contains no diffuse component. If the sample distorts or diffuses the light, then the measured values will depend on the angular size of the light source and the measuring receptor. Specular means only light that is "mirror-reflected" is used in the measurement. The term "diffuse" means that the light is transmitted or reflected in directions other than specular. Total means that all the light is included in the measurement, while directional means that only light reflected or transmitted in specified directions is included in the measurement. Directional also indicates that the "scale is relative to that of the ideally and completely diffusing standard measured under the same conditions of incidence and viewing" (p. 140). Directional values will obviously depend on the angles of both incidence and viewing. Finally, fractional indicates that the light is only a fraction of the incident light. Fractional values will depend on viewing and incidence angles, as well as the solid angle of the receptor. The viewing and incidence angles must be specified.

In a table, E 179 presents the differences between concepts of the regular (specular) and diffuse components of transmittance and reflection. Thus, for reflectance, the specular component is reflected only in the direction of the mirror reflection. It occurs as a function of the smoothness of the surface of the specimen, and typically appears as gloss or shine. The diffuse component of reflection, on the other hand, appears as lightness and arises from cavities or pigment granules in the specimen or from surface roughness. In this case the light is distributed in all directions. Similar distinctions are made for transmittance. Thus, the regular component is simply a continuation of the incident light beam through a clear medium with plane, parallel faces. Because no absorption or scattering of the light takes place, the body appears clear or transparent. Translucency, haziness or turbidity appears when the transmittance is by the diffuse component. In this case, the light is distributed in all directions by scattering or refraction in or on the specimen.

The standard defines four geometric conditions relating to the directions of the incident and viewing beams as well as the field angles for the source and receptor. Specification of the field angles is necessary, along with complete specification of the measuring geometry for factors such as gloss, haze, and transparency. If only specular or diffuse conditions of measurement are being considered, then only the directions of incidence and view need be specified. The standard defines the azimuthal angle as the angle between the source plane and the

normal to the test specimen (relative to the plane containing the normal and the receptor). If the azimuth angle is not specified, the normal to the specimen, the source, and the receptor are assumed to be in the same plane. The rotation angle indicates the orientation of the test specimen in its own plane. The practice also notes that it is usually impossible to differentiate between the specular and diffuse reflection (and transmission). The standard further provides information on the preparation of test specimens.

ASTM D 523 - 85 provides a standard test method for evaluating specular gloss. It defines gloss as the "relative luminous reflectance factor of a specimen in the mirror direction" and the relative luminous reflectance factor as "the ratio of the luminous flux reflected from a specimen to the luminous flux reflected from a standard surface under the same geometric conditions. For the purpose of measuring specular gloss, the standard surface is polished glass" (p. 11). Gloss results when a surface reflects more light in one direction than in another, with the mirror reflection usually having the greatest amount of reflectance (or surface shininess). The standard provides for three measuring geometries (60° , 20° , or 85°) to be used with either a parallel or converging beam glossmeter. Gloss ratings are developed by comparing the specular reflectance from the specimen with that from the black glass standard. Measurements are obtained from a numerical indication proportional to the light flux passing the receptor photocell. The standard provides details of the geometry of the measuring conditions, including source, receptor, specimen and standard. ASTM E 429-78 provides another procedure for measuring metallic surfaces using an integrating sphere, while E 430 - 78 provides for the use of a goniophotometer to measure gloss (particularly on metals). The latter standard defines six characteristics of gloss, ranging from specular gloss and sheen to distinctness of image and reflection haze, to directionality and texture.

A procedure for determining a haze index using two specular gloss measurements is described in ASTM D 4039. The scope of the method states that the method "is particularly useful for evaluating the haze in clear finishes on nonglossy substrates, and the haze in reflected images produced by the surfaces of opaque glossy pigmented finishes."

4. MEASUREMENT OF OTHER SURFACE PROPERTIES

In addition to color and geometric properties, procedures to characterize other surface properties (which affect both the chromatic and geometric appearance properties) have been developed. These procedures include methods of measuring chalking (ASTM D 659) and evaluating the degree of surface disfigurement due to fungal growth or soil and dirt accumulation

(ASTM D 3274). A chalk rating is determined by rubbing piece of felt against the coating in a standardized way and comparing the appearance of the felt with a set of pictorial standards. Extent of surface disfigurement is also determined using a pictorial comparison standard.

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11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here) <p>Research in building materials has increasingly been focused upon procedures for service life prediction. For coatings, improved service life prediction will aid in the effective selection and use of materials and in the development of cost-effective maintenance strategies. However, quantitative measures of degradation are essential in predicting service life. Standard procedures are available to quantitatively measure small changes in the appearance properties of coatings, one of the two primary functions of coatings, the other being protection. However, quantitative measurements of early changes associated with the protective function usually are not possible. Hence, the objective of this report is to ascertain, based upon the literature, whether changes in appearance properties of coatings can be used to predict changes in the protective properties of the film. It was concluded, that for the most part, changes in appearance properties are not related to changes in the protective properties of a coating film.</p>			
12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons) appearance; coatings; durability; measurement; paint; service life			
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